

# Time-Dependent Perturbation Theory and Molecular Spectroscopy

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## I. TIME-DEPENDENT PERTURBATION THEORY

### A. Time-dependent formulation

In Sec. I.B of the Chapter on [molecular electronic structure](#) we considered time-independent perturbation theory. Here, we will treat the case of a time-dependent perturbation, namely

$$H(x, t) = H_0(x) + H'(x, t) = H_0(x, t) + V(x, t)$$

where  $x$  designates all the coordinates. In the section on time-independent perturbation theory in the Chapter on [approximation methods](#) we did not specifically designate the coordinates. Here, we shall designate all the spatial coordinates, collectively, by  $q$ , to distinguish them from the time  $t$ . It is usual to denote the time-dependent perturbation as  $V(q, t)$ . As in [Chapter 1](#), we denote the the time-independent eigenfunctions of  $H_0$  as  $\phi_n^{(0)}(q)$ . In fact, these zeroth-order functions do depend on time, which we have hitherto ignored.

Consider the zeroth-order time-dependent Schrodinger equation

$$i\hbar \frac{\partial \Phi_n(q, t)}{\partial t} = H_0(q) \Phi_n(q, t)$$

Whenever the zeroth-order Hamiltonian is independent of time, we can write the time-dependence as

$$\Phi_n^{(0)}(q, t) = \exp(-i\omega_n^{(0)}t) \phi_n^{(0)}(q)$$

where  $\omega_n^{(0)} = E_n^{(0)}/\hbar$ .

We will expand the solution to the full time-dependent Schrodinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi(q, t) = [H_0(q) + V(q, t)] \Psi(q, t)$$

in terms of the time-dependent solutions to  $H_0$ , namely

$$\Psi(q, t) = \sum_n C_n(t) \Phi_n^{(0)}(q, t)$$

Since

$$H_0 \Phi_n^{(0)} = E_n^{(0)} \Phi_n^{(0)}$$

we have

$$H\Psi = \sum_n C_n(t) E_n^{(0)} \Phi_n^{(0)}(q, t) + \sum_n V(q, t) C_n(t) \Phi_n^{(0)}(q, t)$$

We can obtain the expansion coefficients by substitution of this expansion into the time-dependent Schrodinger equation, then premultiplying by one of the  $\Phi_n^{(0)}$  ( $\Phi_m^{(0)}$ , say) and integrating over the spatial coordinates  $q$ . We then use the orthonormality of the  $\phi_n^{(0)}$  to

obtain

$$i\hbar\dot{C}_m(t) = \sum_n C_n(t) \exp(i\omega_{mn}t) \int \phi_m^{(0)*}(q)V(q,t)\phi_n^{(0)}(q)dq \quad (1)$$

Here the dot on top of the  $C$  on the left-hand-side designates differentiation with respect to time, and

$$\omega_{mn} = [E_m^{(0)} - E_n^{(0)}] / \hbar$$

**Problem 1** Derive Eq. (1).

The integral  $\int \phi_m^{(0)*}(q)V(q,t)\phi_n^{(0)}(q)dq$  will be a function of  $t$ , which will designate  $V_{mn}(t)$ . Thus, Eq. (1) becomes

$$i\hbar\dot{C}_m(t) = \sum_k \exp(i\omega_{mk}t)V_{mk}(t)C_k(t)$$

This set of coupled, first-order differential equations in the expansion coefficients can be written in matrix notation as

$$i\hbar\dot{\mathbf{C}}(t) = \mathbf{G}(t)\mathbf{C}(t)$$

where  $G_{mn} = \exp(i\omega_{mn}t)V_{mn}(t)$ .

These equations are solved subject to a choice of the initial boundary conditions. The magnitude of the coefficient  $C_m(t)$  is the probability that the system will be in state  $|m\rangle$  at time  $t$ . For simplicity, let us assume that the system is in state  $|n\rangle$  at the moment the time-dependent perturbation is switched on. Call this time  $t = 0$ , so that  $C_n(0) = 1$  and  $C_m(0) = 0$  for  $m \neq n$ . As time increases, the effect of the perturbation will result in a transfer of amplitude between the states of the system. The total probability will, however, remain constant, so that

$$\sum_n |C_n(t)|^2 = 1$$

## B. First-order solution

If we assume that the loss of amplitude from state  $|1\rangle$  is small, then all the coefficients  $C_m(t)$  will remain small, except  $C_n(t)$ , so that  $|C_m| \ll |C_n|$  for all time. Then,  $C_n(t) \approx 1$

for all time, so that Eq.(1) reduces to

$$i\hbar\dot{C}_m(t) \approx \exp(i\omega_{mn}t)V_{mn}(t)$$

This can be easily integrated to give

$$C_m(t) = -\frac{i}{\hbar} \int_{t_0}^t \exp(i\omega_{mn}\tau)V_{mn}(\tau)d\tau \quad (2)$$

The square of the absolute value of  $C_m(t)$  represents the probability that at time  $t$  the system, initially in state  $|n\rangle$  will be in state  $|m\rangle$ .

### C. Example: Molecular Collisions

Before discussion the interaction of light with matter, we will discuss the case where the time dependent interaction occurs because of a collision between a molecule and an atom. Here  $|n\rangle$  and  $|m\rangle$  represent two states of the molecule. Typically  $V_{mn}(t)$  will be zero when the two collision partners are asymptotically far apart, will increase as the partners approach, attain a maximum at the distance of closest approach, and then return to zero as they recede. In this case the time-dependent perturbation will extend from  $-\infty$  to  $+\infty$ . Furthermore, as shown in Fig. 1, the coupling matrix element will be symmetric about  $t = 0$ , if we define  $t = 0$  as the point of closest approach. Because the perturbation is symmetric with respect to  $t \rightarrow -t$  only the  $\cos(\omega_{mn}t)$  component in the expansion of the exponential in Eq. (2) will contribute. If the difference in energy between levels  $n$  and  $m$  is large, then this factor will be highly oscillatory, as shown in the left panel in Fig. 2. In this case the integration in Eq. (2), which ranges from  $-\infty$  to  $+\infty$ , will average out to nearly zero. Hence, a collision-induced transition will be improbable. However, if the difference in energy is smaller, then this factor will not oscillate, as also shown in the Fig. 2. In this case the integration over time will not average out to zero.

One can summarize this by a rule of thumb: Let  $l$  be the distance between the point of closest approach and the point at which the  $mn$  coupling potential is non-negligible. Further, let  $v$  be the relative velocity of the two collision partners. Then the time of the collision is the time taken for the relative position of the two particles to go from  $-l$  to  $+l$ . This is  $t_c = 2l/v$ . Assume that the collision will be effective in causing a transition provided

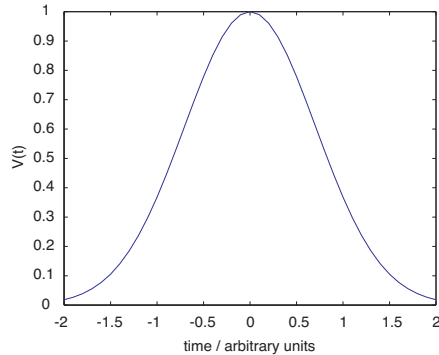


FIG. 1. A model time-dependent interaction typical of a molecular collision. The perturbation is maximal at the distance of closest approach, which we define as  $t = 0$ .

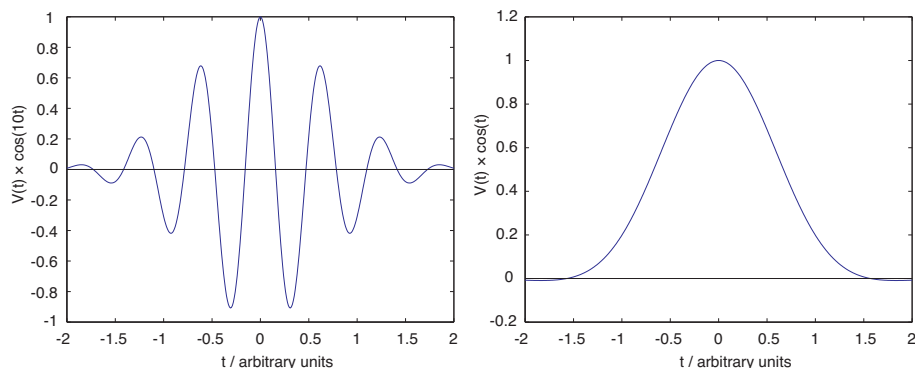


FIG. 2. The product of  $\cos(\omega t)$  multiplied by the perturbation shown in Fig. 1. In the left and right panels the cosine factor is  $\cos(10t)$  and  $\cos(t)$ , respectively.

$\omega_{mn}t_c < \pi$ . This implies that the collision will be effective in causing a transition provided that the energy gap between the initial and final state, call this  $\Delta E_{mn}$  satisfies the inequality

$$|\Delta E_{mn}| < \frac{\hbar\pi v}{2l}$$

**Problem 2** Evaluate the integral in Eq. (11) to derive the last equation.

Consider a idealized collision in which two atoms approach one another at constant velocity  $v$  along a straight line path, defined by the impact parameter  $b$  which is the separation between the particles at the point of closest approach. The probability that a collision will

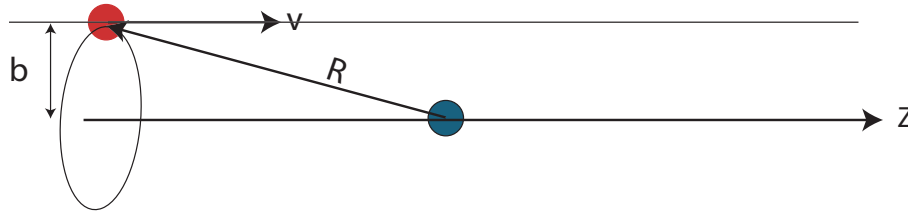


FIG. 3. Idealized collision characterized by the impact parameter  $b$  and the velocity  $v$ . All collisions originating anywhere on a circle of radius  $b$  will be equivalent.

induce a transition into state  $m$  is given by

$$P_{n \rightarrow m}(b, v) = \lim_{t_o \rightarrow -\infty, t \rightarrow \infty} |C_m|^2$$

This probability will depend on the strength of the coupling  $\langle m | H'(x, t) | n \rangle$ , the energy mismatch between the states  $\omega_{mn}$ , and the velocity.

The “cross section”  $\sigma_{mn}(v)$  for the collision induced transition is obtained by integrating  $P_{n \rightarrow m}(b, v)$  over all possible values of the impact parameter, weighted by  $2\pi b$ , which is the circumference of a circle of radius  $b$ . All encounters originating from impact parameters lying on this circle will give rise to equivalent collision-induced transitions. We have

$$\sigma_{mn}(v) = 2\pi \int_0^\infty P_{n \rightarrow m}(b, v) b db \quad (3)$$

**Problem 3** Assume that the coupling matrix element is

$$\langle m | V(z, t) | n \rangle = A_{mn} \exp(-\alpha^2 R^2)$$

where  $R$  is the separation between the two particles and  $A_{mn}$  and  $\alpha$  are constants.

(a) Use trigonometry to determine  $R$  as a function of  $t$ ,  $b$ , and  $v$ . *Hint:* Assume that  $t = 0$  corresponds to the distance of closest approach, at which point  $R = b$ .

(b) Knowing that

$$\int_0^\infty \exp(-a^2 x^2) \cos mx dx = \frac{\sqrt{\pi}}{2a} \exp\left[\frac{-m^2}{4a^2}\right]$$

obtain, and simplify as much as possible, the expression for the cross section  $\sigma_{mn}(v)$ .

In fact, since you are using first-order perturbation theory to calculate  $P_{mn}(b)$ , this approximation will no longer be valid when the calculated expression for  $P_{mn}(b)$  becomes greater than 1. Typically, one replaces the first-order perturbation theory result with

$$\begin{aligned} P_{mn}(b) &= \varepsilon, \text{ when } b < b_o \\ &= \lim_{t_o \rightarrow -\infty, t \rightarrow \infty} |C_m|^2, \text{ when } b \geq b_o \end{aligned} \quad (4)$$

The so-called ‘‘cut-off’’ impact parameter  $b_o$ , inside of which the perturbation theory expression is not valid, is defined by the value of  $b$  for which  $P_{mn}(b, v) = \varepsilon$ , where  $\varepsilon$  is some number less than one.

- (c) Obtain a modified expression for the cross section [Eq. (3)], for the case where  $\varepsilon = 0.5$ .
- (d) Working in atomic units, write a Matlab script to calculate and plot the cross section as a function of velocity (plot the velocity on a logarithmic scale, from  $v = 0.001$  to  $v = 1$ ) for both the un-cut-off and cut-off expressions for  $P_{mn}(b, v)$ , assuming that the parameters are:  $A_{mn} = 0.01$ ,  $\alpha = 1$ , and  $\omega_{mn} = 0.005$ .

## II. INTERACTION OF LIGHT WITH MATTER

One of the most useful applications of time dependent theory is to investigate the rate at which matter will absorb electromagnetic radiation. As shown in Fig. 4, a propagating light

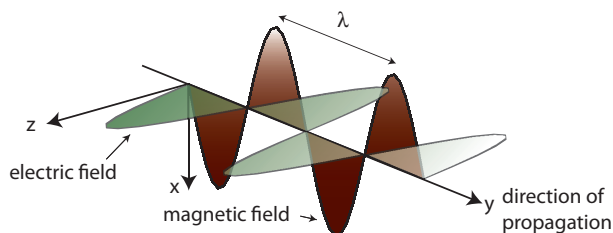


FIG. 4. The crossed electric and magnetic fields of a propagating light wave.

wave contains crossed electric and magnetic fields. We chose our coordinate system so that the electric field is aligned along the  $z$  axis and the the direction of propagation is along the  $x$  axis. The electric and magnetic fields, which are functions of both the distance and the time, are given by

$$\vec{E} = \hat{z}E_o \cos(2\pi\nu t - 2\pi y/\lambda) \quad (5)$$

and

$$\vec{B} = \hat{x}B_o \cos(2\pi\nu t - 2\pi y/\lambda) \quad (6)$$

Here  $\nu$  is the circular frequency. The angular frequency  $\omega$  is  $2\pi\nu$ . The frequency and wavelength are related by  $\nu\lambda = c$ , where  $c$  is the speed of light. The magnitudes of the two fields are related by  $B_o = E_o/c$ .

In a vacuum, or in a non-magnetic material, the energy flux (in  $W/m^2$  or, equivalently,  $Jm^{-2}s^{-1}$ ), called the [Poynting vector](#), is defined by  $\vec{S} = (1/\mu)\vec{E} \times \vec{B}$ , where  $\mu$  is the permeability of the material. (For a vacuum, the permeability is designated  $\mu_o$  and is called the [magnetic constant](#)). From Eqs. (5) and (6), we see that

$$|\vec{S}| = \frac{1}{\mu_o c} |E_o|^2 \cos^2(\omega t - 2\pi z/\lambda).$$

If you integrate over an entire cycle ( $t \rightarrow t + 2\pi/\omega$ ) then, since  $\int_0^{2\pi} \cos^2 \theta d\theta = 1/2$ ,

$$\langle S \rangle = \frac{1}{2\mu_o c} E_o^2 = \frac{\epsilon_o c}{2} E_o^2$$

where  $\epsilon_o$  is the permittivity of free space, also called the [electric constant](#) and  $\epsilon_o\mu_o = c^{-2}$ . The flux is the electromagnetic energy per second impinging on a wall of area  $1m^2$ . If you divide the flux by the velocity (the speed of light), you get a quantity which has units of energy per  $m^3$ . This is the so-called energy density of the radiation field.

$$\rho(\nu) = \frac{\epsilon_o}{2} E_o^2 \quad (7)$$

The interaction of the light wave with matter is due to the electric field of the wave [the interaction with the magnetic field is smaller by  $1/137$  (one divided by the fine-structure constant)]. The force exerted by an electric field on a particle of charge  $Q$  is

$$\vec{F} = Q\vec{E}$$

Since the force is the negative of the gradient of a potential, we see that the interaction of



an electric field polarized in the  $z$  direction (Fig. 4) with a charged particle is governed by the potential

$$V(z) = V_o - QzE_z$$

Without loss of generality we can set the reference potential  $V_o$  equal to zero.

For a collection of particles, the potential is

$$V = -E_z \sum_i Q_i z_i$$

With Eq. (5), we can rewrite this equation as

$$V(y, z, t) = -E_o \sum_i Q_i z_i \cos(\omega t - 2\pi y_i/\lambda)$$

Here  $y_i$  is the position along the  $y$ -axis of the  $i^{\text{th}}$  particle. Since the wavelength of light is typically  $10^3$  times the size of an atomic or small molecular system, over the position of the molecule

$$\cos(\omega t - 2\pi y_i/\lambda) \approx \cos(\omega t - \gamma)$$

where  $\gamma$  is a constant. If we replace  $t$  by  $t + \gamma/\omega$  (which is equivalent to shifting the zero of time, which has not yet been defined), then we find

$$V(y, z, t) \approx V(z, t) = -E_o \sum_i Q_i z_i \cos(\omega t) = -E_o \cos(\omega t) \sum_i Q_i z_i \equiv -E_o \cos(\omega t) \hat{D}_z(\vec{r}, \vec{R}) \quad (8)$$

The quantity under the summation sign (the sum of the position of all the charged particles multiplies by their charges is called the “dipole moment operator”  $\hat{D}$  – in this case we are considering just the  $z$  component of this operator, since the electric field lies along the  $z$  direction.

In electronic state  $\phi_{el}^{(k)}(\vec{r})$  the average of  $\hat{D}_z$ , averaged over the positions of all the electrons is

$$D_z^{(k)}(\vec{R}) = \int \phi_{el}^{(k)*}(\vec{r}) \hat{D}_z(\vec{r}, \vec{R}) \phi_{el}^{(k)}(\vec{r}) d\vec{r}$$

We shall call this the dipole-moment vector. It depends, in the case of a diatomic molecule, on the magnitude and orientation of the molecular axis  $\vec{R}$ . Note that for homonuclear

molecules, or for molecules with inversion symmetry, the dipole-moment vector will vanish by symmetry. Similarly the matrix element of  $\mathcal{D}_z(\vec{r}, \vec{R})$  between two different electronic states, namely

$$D_z^{(k,l)}(\vec{R}) = \int \phi_{el}^{(k)}(\vec{r})^* \hat{D}_z(\vec{r}, \vec{R}) \phi_{el}^{(l)}(\vec{r}) d\vec{r} \quad (9)$$

is called the electronic transition dipole moment vector.

### A. Absorption of radiation by matter

Consider two different vibronic states of a molecule, with wavefunctions given by Eq. (29) of Chapter 3, namely

$$\psi_{k,v,j,m}(X, Y, Z) = Y_{jm}(\Theta, \Phi) \chi_{vj}(R) \chi_{el}^{(k)}(\vec{r}; R)$$

Hereafter, in this Chapter we shall use the same notation that spectroscopists use: designating with primes and double primes the quantum numbers and labels of the final and initial systems. For a system initially in state  $|k''v''j''m''\rangle$  at time  $t = 0$ , the probability of being in state  $|k'v'j'm'\rangle$  at time  $t$  is  $|C_{k'v'j'm',k''v''j''m''}(t)|^2$ . Here, we have added an additional subscript to the expression for the time-dependent probability amplitude  $C$ , so that  $C_{mn}$  will designate the probability amplitude of being in state  $m$  for a system which was initially entirely in state  $n$ . More simply, if we designate the initial  $(k''v''j''m'')$  and final  $(k'v'j'm')$  states by the single indices  $i$  and  $f$ , the probability of finding at time  $t$  the system in state  $f$  is  $|C_{fi}(t)|^2$ .

To first order in perturbation theory, the transition amplitude is given by Eq. (2), applied to the case when the time dependent perturbation is given by Eq. (8). We have

$$C_{fi} = -\frac{i}{\hbar} E_o \langle \psi_{k'v'j'm'} | \hat{D}_z(\vec{r}, \vec{R}) | \psi_{k''v''j''m''} \rangle \int_0^t \cos(\omega\tau) \exp(i\omega_{fi}\tau) d\tau$$

Let us define

$$M_{fi} \equiv \langle \psi_{k'v'j'm'} | \hat{D}_z(\vec{r}, \vec{R}) | \psi_{k''v''j''m''} \rangle \quad (10)$$

so that we can write

$$C_{fi} = \frac{-i}{\hbar} E_o M_{fi} \int_0^t \cos(\omega\tau) \exp(i\omega_{fi}\tau) d\tau \quad (11)$$

Integration gives

$$C_{fi} = -\frac{i}{2\hbar} E_o M_{fi} \left[ \frac{e^{i(\omega_{fi}-\omega)t} - 1}{\omega_{fi} - \omega} + \frac{e^{i(\omega_{fi}+\omega)t} - 1}{\omega_{fi} + \omega} \right]$$

**Problem 4** Evaluate the integral in Eq. (11) to derive the last equation.

Typically, the frequencies  $\omega_{fi}$  are large, on the order of  $10^{11}$  or greater. If state  $f$  is higher in energy than state  $i$ , then the denominator of the 2nd term in square brackets will be much larger than that of the first term. Let's then retain just the first term in square brackets, then take the absolute value squared of the resulting expression for  $C_{fi}$ , and use the expansion

$$\frac{|e^{ixt}|^2}{x^2} = \frac{1}{x^2} (2 - 2 \cos xt) = \frac{4 \sin^2(xt/2)}{x^2}$$

We then get

$$|C_{fi}(t)|^2 = \left( \frac{E_o |M_{fi}|}{\hbar} \right)^2 \frac{\sin^2 \frac{1}{2}(\omega_{fi} - \omega)t}{(\omega_{fi} - \omega)^2}$$

We can replace the angular frequency  $\omega$  with the circular frequency  $\nu$

$$|C_{fi}(t)|^2 = \left( \frac{E_o M_{fi}}{\hbar} \right)^2 \frac{\sin^2 \pi(\nu_{fi} - \nu)t}{4\pi^2(\nu_{fi} - \nu)^2}$$

and also replace  $E_o^2$  by the radiation density [Eq. (7)], obtaining, finally

$$|C_{fi}(t)|^2 = \frac{2\rho_z(\nu)}{\epsilon_o} \left( \frac{|M_{fi}|}{\hbar} \right)^2 \frac{\sin^2 \pi(\nu_{fi} - \nu)t}{4\pi^2(\nu_{fi} - \nu)^2}$$

Here, we have included a subscript  $x$  on the radiation density, to designate that this is the electromagnetic energy density associated with the fraction of the photons moving in the  $\hat{z}$  direction. For a volume in which the distribution of radiation is isotropic, the density associated with light waves propagating forward or backward in any one of the three Cartesian directions is one-third the total radiation density, so that  $\rho_x(\nu) = \rho(\nu)/3$ . In terms, then, of  $\rho(\nu)$ , we have

$$|C_{fi}(t)|^2 = \frac{2\rho(\nu) |M_{fi}|^2}{3\epsilon_o \hbar^2} \frac{\sin^2 \pi(\nu_{fi} - \nu)t}{4\pi^2(\nu_{fi} - \nu)^2}$$

**Problem 5** Make the variable substitution  $x = \pi(\nu_{fi} - \nu)t$  to transform this equation to

$$|C_{fi}(t)|^2 = \frac{t^2 \rho(\nu) |M_{fi}|^2}{6\pi\epsilon_0 \hbar^2} \frac{\sin^2 x}{x^2}$$

The dependence on  $x$  of the function  $\sin^2(x)/x^2$  is shown in Fig. 5. As you can see, this

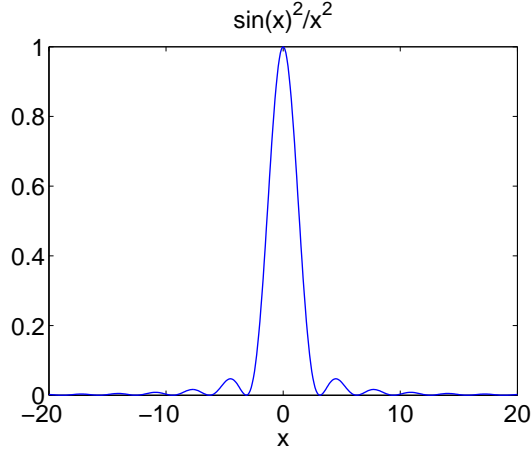


FIG. 5. Dependence on  $x$  of the function  $\sin^2(x)/x^2$ .

function is sharply peaked at  $x = 0$ . The important contribution is limited to  $-\pi < x < \pi$ . Once  $t$  is larger than  $1/|\nu - \nu_{if}|$ , then  $|C_{fi}(t)|^2$  will be quite small. At times longer than this limit, only light of frequency  $\nu \cong \nu_{if}$  will make any contribution to transferring population from state  $i$  to state  $f$ . This leads to the statement, first postulated by Bohr in his model of the H atom, that an atom will undergo a transition from level  $i$  to level  $f$  only when exposed to frequency of  $\nu = (E_f - E_i)/h$ . However, at very short times, absorption can occur over a small, but finite, range of frequencies centered about  $\nu = \nu_{fi}$ .

We now integrate the expression for  $|C_{fi}(t)|^2$  over all frequencies. This will give the total contribution of the radiation field of density  $\rho(\nu)$  to population transfer into state  $f$ . Let us designate this  $\langle |C_{fi}(t)|^2 \rangle$ . Since  $dx = -\pi t d\nu$ , we have

$$\langle |C_{fi}(t)|^2 \rangle = \frac{t^2 |M_{fi}|^2}{6\epsilon_0 \hbar^2} \int_0^\infty \frac{\rho(\nu) \sin^2 x}{x^2} d\nu \quad (12)$$

$$= -\frac{t |M_{fi}|^2}{6\pi\epsilon_0 \hbar^2} \int_{\pi\nu_{fi}t}^{-\infty} \frac{\rho(\nu) \sin^2 x}{x^2} dx \quad (13)$$

Since typical frequencies  $\nu_{fi}$  are very large, you can replace the lower limit of integration by

$+\infty$ . Reversing the order of integration will get rid of the minus sign out front, leading to

$$\langle |C_{fi}(t)|^2 \rangle = \frac{t |M_{fi}|^2}{6\pi\epsilon_o\hbar^2} \int_{-\infty}^{+\infty} \frac{\rho(x) \sin^2 x}{x^2} dx$$

If we further assume that the photon density is constant over the range sampled by the integral, so that

$$\rho(x) \approx \rho(x=0) = \rho(\nu = \nu_{fi}) = \rho(\nu_{fi}),$$

then you can take the density out from beneath the integral sign, obtaining

$$\langle |C_{fi}(t)|^2 \rangle = \frac{t\rho(\nu_{fi}) |M_{fi}|^2}{6\pi\epsilon_o\hbar^2} \int_{-\infty}^{+\infty} \frac{\sin^2 x}{x^2} dx \quad (14)$$

$$= \frac{t\rho(\nu_{fi}) |M_{fi}|^2}{6\epsilon_o\hbar^2} \quad (15)$$

The derivative of the population in state  $f$  with respect to time is the rate as which the light field populates level  $f$  starting with the system in level  $i$ . This rate is proportional to the radiation density at frequency  $\nu = \nu_{if}$ . The constant of proportionality, called the Einstein B coefficients, is

$$B_{fi} = \frac{|M_{fi}|^2}{6\epsilon_o\hbar^2} \quad (16)$$

If level  $f$  lies higher than level  $i$ , then this  $B$ -coefficient is the rate for stimulated absorption (absorption of energy stimulated by the electromagnetic field). It is proportional to the square of the matrix element of the dipole operator between states  $i$  and  $f$ . Since the absolute value squared of the matrix element of any physical operator is independent of the order of the initial and final states, it is also clear that the rate of stimulated absorption (level  $i$  to level  $f$ ) is identical to the rate of stimulated emission (level  $f$  to level  $i$ ).

## B. Spontaneous emission

Let the total number of molecules in levels  $i$  and  $f$  be  $N_i$  and  $N_f$ . The overall rate of stimulated absorption (energy absorbed per unit time) is

$$N_i\rho(\nu_{fi})B_{fi} \quad (17)$$

while the overall rate of stimulated emission (energy emitted per unit time) is

$$N_f \rho(\nu_{if}) B_{if}$$

Obviously,  $\rho(\nu_{if}) = \rho(\nu_{fi})$ .

However, equilibrium statistical mechanics demonstrates that the number of molecules in the lower state must be larger than the number in a higher state. Specifically, at equilibrium

$$N_f/N_i = \exp(-h\nu_{fi}/k_B T), \quad (18)$$

where  $k_B$  is the Boltzmann constant.

Since the number of molecules in the lower energy state is greater, the overall rate of stimulated absorption will be greater than the overall rate of stimulated emission, so that, eventually, the number of molecules in the two states will equilibrate, which is contrary to the predictions of equilibrium statistical mechanics.

To resolve this paradox, Einstein proposed the existence of another process, *spontaneous* emission. He postulated that there exists a small probability for an excited molecule (or atom) to release a photon even in the absence of an electromagnetic field. The rate of spontaneous emission, which is denoted  $A_{fi}$ , will be thus independent of the energy density of the radiation field. Consequently, the total rate of energy emission from the upper state is

$$N_f \rho(\nu_{fi}) B_{fi} + A_{fi} N_f = N_f [A_{fi} + \rho(\nu_{if}) N_i B_{fi}] \quad (19)$$

This must be equal to the overall rate of energy absorption from the lower state, given by Eq. (17).

**Problem 6** Assume that at equilibrium the overall rate of energy absorption must equal the overall rate of energy emission, so that Eq. (17) must equal Eq. (19). Using this equality and using Eq. (18) to relate  $N_f$  and  $N_i$ , show how you can eliminate these populations to obtain

$$A = B\rho(\nu) [\exp(h\nu/k_B T) - 1]$$

Here, we have dropped the  $fi$  and  $if$  subscripts, which are no longer needed. Planck showed that in a black-body cavity at equilibrium at temperature  $T$  the energy density at frequency

$\nu$  is

$$\rho(\nu, T) = \frac{8\pi h\nu^3}{c^3} \frac{1}{\exp(h\nu/k_B T) - 1}$$

From these last two equations show that the Einstein  $A$  coefficient is given by

$$A_{fi} = \frac{8\pi h\nu_{fi}^3}{c^3} B_{fi} = \frac{8\pi^2 \nu_{fi}^3 |M_{fi}|^2}{3\hbar\epsilon_0 c^3} \quad (20)$$

Note that the  $A$  coefficient depends on the *cube* of the frequency. Spontaneous emission is much more probable for ultraviolet transitions than for microwave transitions.

### C. Selection Rules: Transitions within the same electronic state

Both the Einstein  $A$  and  $B$  coefficients depend on the square of the matrix element of the dipole-moment operator, given by Eq. (10). We can distinguish two cases: (a) transitions within the same electronic states ( $l = k$ ) and (b) transitions between different electronic states.

For transitions within the same electronic state, we have

$$M_{fi} = \int_0^{2\pi} \int_0^\pi Y_{j'm'}(\Theta, \Phi)^* Y_{j''m''}(\Theta, \Phi) \sin \Theta d\Theta d\Phi \int_0^\infty \chi_{v'j'} D_z^{(k)}(\vec{R}) \chi_{v''j''} R^2 dR \quad (21)$$

For a diatomic molecule, the dipole moment vector  $D_z^{(k)}(\vec{R})$  must lie along the molecular axis, by symmetry. Thus

$$D_z^{(k)}(\vec{R}) = \cos \Theta D^{(k)}(R) \quad (22)$$

where  $\Theta$  is the angle between the molecular axis  $\vec{R}$  and the  $z$ -axis, and the scalar  $D^{(k)}(R)$  is called the “dipole-moment function.” Thus, if the molecule is aligned so that the bond axis points along the direction of the electric field, then  $\Theta = 0$  so that the electric field of the radiation sees the full molecular dipole. If, by contrast, the bond axis points perpendicular to the direction of propagation ( $\Theta = 90^\circ$ ), the molecule will not absorb radiation. Equation (21) then becomes

$$M_{fi} = D_{v'j',v''j''}^{(k)} \int_0^{2\pi} \int_0^\pi Y_{j'm'}(\Theta, \Phi)^* \cos \Theta Y_{j''m''}(\Theta, \Phi) \sin \Theta d\Theta d\Phi \quad (23)$$

where

$$D_{v'j',v''j''}^{(k)} = \int_0^\infty \chi_{v'j'} D^{(k)}(R) \chi_{v''j''} R^2 dR \quad (24)$$

### 1. Rotational Selection Rules

The magnitude of these two integrals (over  $R$  and over  $\Theta$  and  $\Phi$ ) will then, from Eqs. (16) and (20), govern the efficiency of the transition from state  $|k''v''j''m''\rangle$  to state  $|k'v'j'm'\rangle$ . Let us consider first the angular integral. Since the  $\Phi$  dependence of the spherical harmonics is  $\exp(im\Phi)$  and since in Eq. (23) the azimuthal angle appears only in the spherical harmonics, integration over  $\Phi$  will give zero unless  $m' = m''$ . This restriction is one of a number of optical “selection rules”, namely that in a transition induced by linearly polarized light (light in which the electric field oscillates in a plane, as shown in Fig. 4,  $\Delta m = 0$ .[1]

With this restriction, the integral over  $\Theta$  then is

$$\int_0^\pi Y_{j'm'}(\Theta, \Phi)^* \cos \Theta Y_{j''m'}(\Theta, \Phi) \sin \Theta d\Theta \quad (25)$$

In fact, the spherical harmonic  $Y_{10}$  is proportional to  $\cos \Theta$

$$Y_{10}(\Theta) = \left(\frac{1}{2\pi}\right)^{1/2} \cos \Theta$$

so that the integral over  $\Theta$  can be rewritten as

$$(2\pi)^{1/2} \int_0^\pi Y_{j'm'}^*(\Theta, \Phi) Y_{10}(\Theta, \Phi) Y_{j''m'}(\Theta, \Phi) \sin \Theta d\Theta \quad (26)$$

This integral vanishes unless (Selection rule 2) [2]

$$j' = j'' \pm 1 \quad (27)$$

If this selection rule is met, then the integral has the value [2]

$$\int_0^\pi Y_{j''+1,m}^* Y_{10} Y_{j''m} \sin \Theta d\Theta = (-1)^{-m} \left[ \frac{3(j''+m+1)(j''-m+1)}{2\pi(2j''+1)(2j''+3)} \right]^{1/2} \quad (28)$$

Since the Einstein A and B coefficients are proportional to the absolute value squared of



$M_{fi}$ , we see that the dependence on the rotational quantum number will be

$$B_{j''+1 \leftarrow j''} \sim \frac{(j'' + m + 1)(j'' - m + 1)}{(2j'' + 1)(2j'' + 3)}$$

## 2. Vibrational Selection Rules

In the case where  $j' = j'' \pm 1$  and  $m' = m''$ , so that the rotational selection rules are satisfied, we then have to consider the vibrational integral of the dipole moment function, Eq. (24). To evaluate this integral, we expand the dipole moment function about  $R = R_e$ , namely

$$D^{(k)}(R) \approx D^{(k)}(R_e) + \frac{dD^{(k)}}{dR_e}(R - R_e) + \mathcal{O}[(R - R_e)^2] \quad (29)$$

where

$$\frac{dD^{(k)}}{dR_e} \equiv \left. \frac{dD^{(k)}(R)}{dR} \right|_{R=R_e}$$

Also, we shall assume that the vibrational wavefunctions are harmonic oscillator functions, namely

$$\chi_{vj}(R) = \chi_v^{\text{HO}}(R - R_e)$$

The harmonic oscillator functions satisfy the same recursion relation as the [Hermite polynomials](#), namely

$$xH_n(x) = H_{n+1}(x) + nH_{n-1}(x)$$

so that, from the orthogonality of the harmonic oscillator functions

$$\langle \chi_{v''}^{\text{HO}} | D^{(k)}(R_e) | \chi_{v''}^{\text{HO}} \rangle = D^{(k)}(R_e) \quad (30)$$

$$\langle \chi_{v'}^{\text{HO}} | D^{(k)}(R_e) | \chi_{v''}^{\text{HO}} \rangle = 0, \quad v' \neq v''$$

$$\begin{aligned} \langle \chi_{v'}^{\text{HO}} | \frac{dD^{(k)}(R)}{dR}(R - R_e) | \chi_{v''}^{\text{HO}} \rangle &= 0, \quad v' = v'' \\ &= \left. \frac{dD^{(k)}(R)}{dR} \right|_{R=R_e}, \quad v' = v'' + 1 \\ &= v'' \left. \frac{dD^{(k)}(R)}{dR} \right|_{R=R_e}, \quad v' = v'' - 1 \end{aligned}$$

$$= 0, \text{ otherwise} \quad (31)$$

Thus, the vibrational selection rule is  $\Delta v = 0, \pm 1$ . This selection rule is rigorous provided that higher-order terms in the expansion of the dipole-moment function [Eq. (29)] are negligible. In reality, transitions with  $\Delta v > 1$  are weakly allowed. These are called “overtone” transitions.

#### D. Pure Rotation Transitions

Consider first transitions within a given electronic state for which the vibrational quantum number is *unchanged*. The corresponding spectrum corresponds to pure rotational transitions. The  $i$  to  $f$  coupling matrix element [Eq. (21)] vanishes unless  $j' = j'' \pm 1$  and is proportional to the dipole moment function [Eq. (22)] evaluated at  $R = R_e$  [Eq. (30)]. As mentioned earlier, this is called the molecular dipole moment. [3] Thus, if the molecule is homonuclear, in which case the dipole moment vanishes, rotational transitions can not occur.

At equilibrium the relative population in rotational level  $jm$  is given by a Boltzmann distribution

$$P(jm, T) = \exp(-\varepsilon_j/k_B T) / z_r \quad (32)$$

where,  $\varepsilon_j \approx B_v j(j+1)$ , where  $B_v$  is the rotational constant in the  $v^{\text{th}}$  vibrational manifold, and  $z_r$  is the rotational partition function

$$z_r = \sum_{j=0}^{\infty} \sum_{m=-j}^j \exp(-\varepsilon_j/k_B T)$$

Because the energies of the rotational levels are independent of the projection quantum number  $m$ , we can sum over the  $m$  states, obtaining the [well-known expression](#)

$$z_r = \sum_{j=0}^{\infty} (2j+1) \exp(-\varepsilon_j/k_B T) \quad (33)$$

**Problem 7** Show that a temperatures for which  $\delta\varepsilon_j$  (the spacing between rotational levels)

is significantly than  $k_B T$ , the rotational partition function can be written as

$$\lim_{k_B T \gg \delta \epsilon} z_r = k_B T / B_r$$

where the rotational constant,  $B_r$  is measured in energy units. In other words, the rotational partition functions, which is the effective total number of energetically-accessible rotational states at temperature  $T$ , is just the ratio of the thermal energy to the rotational spacing.

For CO, Table I gives the important spectroscopic constants (in  $\text{cm}^{-1}$ ). Write a Matlab

TABLE I. Spectroscopic constants for the CO molecule.

Constant <sup>a</sup>	$E$ ( $\text{cm}^{-1}$ )
$\omega_e$	2169.814
$\omega_e x_e$	13.2883
$B_e$	1.93128
$\alpha_e$	0.01750

<sup>a</sup> See Eq. (44) of Chapter 3.

script to carry out the summation in Eq. (33) and graph the true rotational partition function and the high-temperature limit over the range  $10 < T < 500$ .

Consider a transition out of level  $jm$  into level  $j \pm 1, m$  (remember that for linearly polarized light  $\Delta m = 0$ ). At thermal equilibrium, the population in level  $j - 1, m$  will be greater than in level  $jm$ . Consequently, stimulated emission will not occur.

The Einstein  $B$  coefficient [Eq. (16)] is proportional to the square of the absolute value of the  $i \rightarrow f$  coupling matrix element, which is, itself, proportional to the matrix element of the dipole moment function between levels  $j''m''$  and  $j'm'$ . Thus, from Eqs. (28) and (30), the overall rate at which radiation is absorbed in the transition between the initial level  $j''m''$  and the final level  $j'm'$  is

$$\begin{aligned} \mathcal{R}(j'm' \leftarrow j''m''; \nu_{j'm',j''m''}) &= \rho(\nu_{j'm',j''m''}) N_{j''m''}(T) B(j'm' \leftarrow j''m''; \nu_{j'm',j''m''}) \\ &= \frac{\delta_{m'm''} \rho(\nu_{j'm',j''m''}) N_{j''m''}(T)}{24\pi\epsilon_0 \hbar^2} D^{(k)}(R_e)^2 \frac{(j+m+1)(j-m+1)}{(2j+1)(2j+3)} \end{aligned} \quad (34)$$

Here,  $N_{j''m''}(T)$  is number of molecules in state  $j''m''$  at temperature  $T$ . This is the total number of molecules multiplied by the relative number in state  $j''m''$ , Eq. (32)], namely

$$N_{j''m''} = N \exp(-\varepsilon_{j''m''}/k_B T)$$

where  $N$  is the total number of molecules.

Note the left arrow in the preceding equation. Spectroscopists designate a transition with the notation *final state*  $\leftarrow$  *initial state*. Also, in Eq. (34) the Kronecker delta in the 2nd line reflects the vanishing of the  $B$  coefficient unless  $m' = m''$  which is a consequence of the rotational selection rule that  $\Delta m = 0, \pm 1$ .

In the absence of external fields, the energy of the rotational levels is independent of the projection quantum number. Thus, the overall absorption of radiation at frequency  $\nu_{j'j''}$  is proportional to

$$\mathcal{R}(j' \leftarrow j''; \nu_{j'j''}) \sim \sum_{m''=-j''}^{j''} N(j''m'') \frac{(j'' + m'' + 1)(j'' - m'' + 1)}{(2j'' + 1)(2j'' + 3)}$$

**Problem 8** Write a Matlab script to show that

$$\sum_{m''=-j''}^{j''} N(j''m'') \frac{(j'' + m'' + 1)(j'' - m'' + 1)}{(2j'' + 1)(2j'' + 3)} = N(j'' + 1) \exp(-\varepsilon_{j''}/k_B T) / z_r \quad (35)$$

The rotational levels of a diatomic are, to very high precision (see Sec. V.B of Chapter 3)

$$\varepsilon_j = B_v j(j + 1) = [B_e - \alpha_e(v + 1/2)] j(j + 1)$$

Thus, the pure rotational spectrum of a molecule consists of a number of lines at positions  $2B_v, 4B_v, \dots, 2(j'' + 1)B_v$  corresponding to the transitions  $1 \leftarrow 0, 2 \leftarrow 1, \dots, j'' + 1 \leftarrow j''$ , respectively. The relative intensities of these lines will be  $(j'' + 1) \exp[-j''(j'' + 1)B_v/k_B T]$ . In calculating these intensities, it is convenient to remember that an energy in wavenumbers can be converted to an equivalent thermal temperature by multiplication by 1.4388. In other words

$$\Delta E(J) / [k_B(\text{J/K})T(\text{K})] = \Delta E(\text{cm}^{-1}) \times 1.4388 / T(\text{K})$$

Consider the case of CO ( $B_{v=0} = 1.9225 \text{ cm}^{-1}$ , see Tab. I) at a temperature of 200 K. Figure 6 shows the simulated pure-rotational spectrum. In any experiment, the observed lines will be broadened beyond an ideal stick spectrum, because of instrumental effects or by Doppler broadening. To simulate a broadened spectrum, we can convolute each line with a Gaussian function, namely

$$I(\nu) = \sum_{j''} (j'' + 1) \exp(-\varepsilon_{j''}/k_B T) \exp[-\alpha(\nu - \nu_{j''j'})^2] \quad (36)$$

Spectral broadening is usually described in terms of the **full-width at half-maximum** (FWHM) of the lines. If we assume that the broadening is the same for all the rotational lines, then,

$$\alpha = 2/\delta_\nu^2 \quad (37)$$

where  $\delta_\nu$  is the full width at half max of the lines.

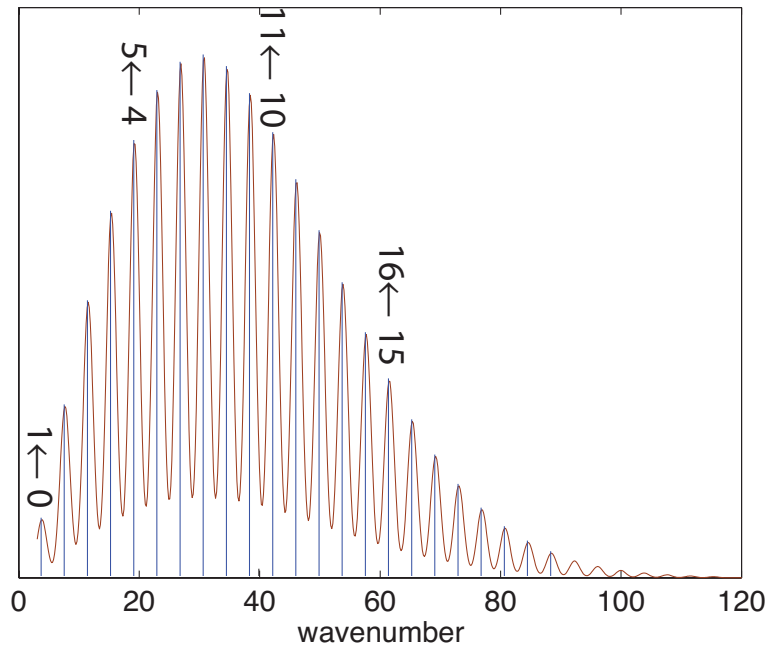


FIG. 6. Stick spectrum of the pure-rotational spectrum of CO( $v = 0$ ) at  $T = 200\text{K}$ . The spectral assignment (initial and final rotational quantum numbers) is also shown. The red curve is the simulation of spectral broadening, obtained by convoluting with a Gaussian function of  $2 \text{ cm}^{-1}$  FWHM, see Eq. (36).

### E. Vibration-Rotation Transitions

We consider now transitions between two different vibrational manifolds ( $v' \neq v''$ ). Because of the vibrational selection rule, to a good approximation  $v' = v'' \pm 1$ . The coupling, and hence the strength of the absorption, is now related not to the dipole moment at  $R = R_e$ , but to the first derivative of the dipole-moment function at  $R = R_e$ , as seen in Eq. (31). Consider, specifically, transitions from a lower to a higher vibrational manifold ( $v' = v'' + 1$ ). There are two sets (or “branches”) of rotational transitions: those with  $j' = j'' + 1$  and those with  $j' = j'' - 1$ . These are called, respectively, the “R branch” and the “P branch”. The energy gap is given by

$$\begin{aligned} \Delta_E &\equiv \varepsilon_{v'j'} - \varepsilon_{v''j''} = \omega_e - 2(v'' + 1)\omega_e x_e + B_1(j'' + 1)(j'' + 2) - B_0j''(j'' + 1), \quad j' = j'' + 1 \\ &= \omega_e - 2(v'' + 1)\omega_e x_e + B_1j''(j'' - 1) - B_0j''(j'' + 1), \quad j' = j'' - 1 \end{aligned} \quad (38)$$

Here  $B_0 = B_e - \alpha_e/2$  and  $B_1 = B_e - 3\alpha_e/2$ . If one neglects the vibration-rotational coupling term  $\alpha_e$ , then the R-branch lines start at the  $1 \leftarrow 0$  line at a transition energy of

$$\Delta_E(1 \leftarrow 0) = \omega_e - 2(v'' + 1)\omega_e x_e + 2B_e$$

Then, exactly as in the case of the pure rotation transitions treated earlier in Sec. IID, the lines originating in  $j'' = 2, 3, \dots$  etc. appear at higher and higher energy, each separated by  $2B_e$ . For the P branch, the first line corresponds to  $0 \leftarrow 1$ . The higher  $j$  lines then appear at lower and lower energy, again each separated by  $2B_e$ . The intensities of the R-branch lines are given by Eq. (28). The corresponding expression for the P-branch lines is

$$\int_0^\pi Y_{j''-1,m}^* Y_{10} Y_{j'',m} \sin \Theta d\Theta = (-1)^{-m} \left[ \frac{3(j'' + m)(j'' - m)}{2\pi(2j'' - 1)(2j'' + 1)} \right]^{1/2} \quad (39)$$

**Problem 9** Similar to problem 8, write a Matlab script to show that

$$\sum_{m=-j''}^{j''} N(j''m'') \frac{(j'' + m)(j'' - m)}{(2j'' - 1)(2j'' + 1)} = Nj'' \exp(-\varepsilon_{j''}/k_B T) / z_r \quad (40)$$

Comparing Eqs. (35) and (40), we see that the relative intensities of the R- and P-branch lines originating from level  $j''$  in the vibrational ground state is  $(j'' + 1) : j''$ . Further, the sum of the intensity of the R- and P-branch lines originating from level  $j''$  in the vibrational ground state is  $(2j'' + 1) \exp(-\varepsilon_{j''}/k_B T)$ . This is exactly the overall population (summed over all the degenerate project states) associated with rotational level  $j''$  at temperature  $T$ .

For CO, Figure 7 displays the simulated spectrum for the  $v = 1 \leftarrow 0$  vibration-rotation transition in the ground electronic state of CO.

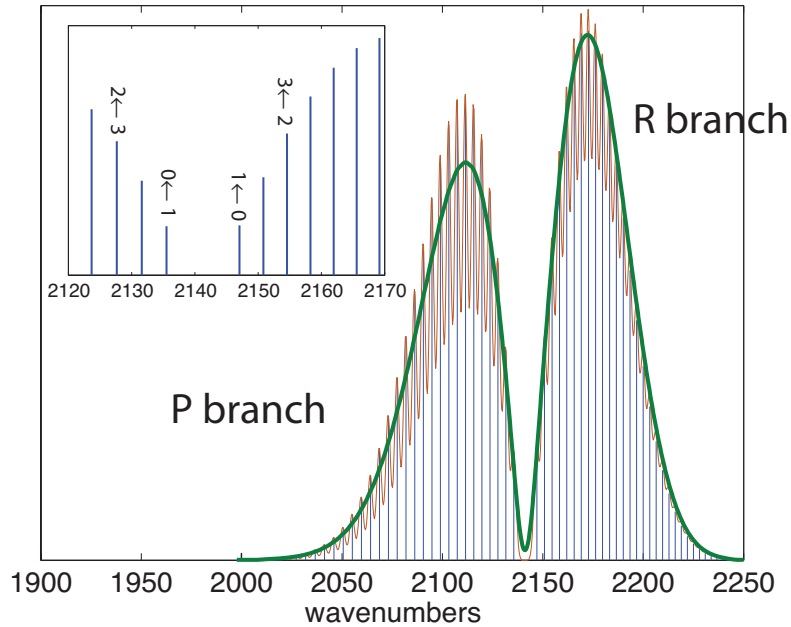


FIG. 7. Infrared absorption spectrum of  $\text{CO}(v=0)$  at  $T=200\text{K}$ . The blue lines indicate the stick spectrum, while the orange and green curves indicated the anticipated spectrum broadened by a Gaussian instrument function with FWHM of, respectively, 3 and 6  $\text{cm}^{-1}$ . The spectral assignment (initial and final rotational quantum numbers) is shown in the inset.

**Problem 10** Examination of the figure and Eq. (38) reveals that there is a gap, which is called the “band origin”, between the P- and R-branches, of width  $\approx 4B_e$ . Show that the location of the center of this gap corresponds to the energy of the vibrationless  $v''=0, j''=0 \rightarrow v'=1, j'=0$ .

We also observe that convolution can totally remove all structure in the spectrum, provided that the FWHM of the instrument function is greater than the spacing between the

vibration-rotation transitions. This is indicated by the thick green line in Fig. 7. Only the broad envelopes of the P and R branches remain.

### 1. Q branches

For molecules in which the ground state has non-zero electronic orbital and/or spin electronic angular momentum, the rotational motion of the molecule is described not by spherical harmonics but by more complex functions, called reduced rotation matrix elements.[2] In this case the angular integration of Eq. (26) no longer vanishes when  $j' = j''$ . Thus, transitions with  $j' = j''$  can occur. This is called the “Q branch”. The transition energy is

$$\Delta_E^{(Q)} = \omega_e - 2(v'' + 1)\omega_e x_e - \alpha_e j''(j'' + 1)$$

Since the constant  $\alpha_e$  is usually small, all the Q-branch lines tend to lie at the same energy. In addition, the intensity of the Q-branch lines, if a Q-branch exists, are approximately equal to the sum of P- and R-branch intensities. Figure 8 shows the CO spectrum with the addition of a Q branch. This is only hypothetical, since the ground electronic state of CO is  $^1\Sigma^+$ .

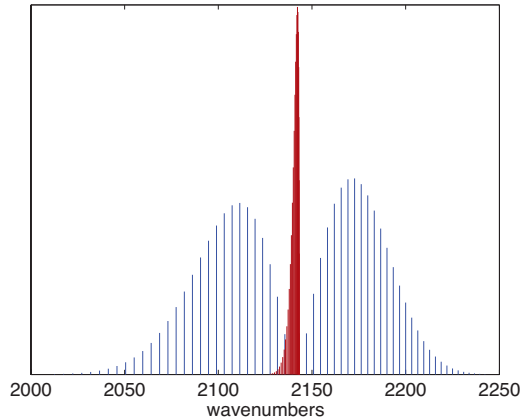


FIG. 8. Simulated Infrared absorption spectrum of CO( $v = 0$ ) at  $T = 200\text{K}$  with the addition of a hypothetical Q branch (red).



## F. Electronic-Rotational-Vibrational Transitions

Consider a situation in which a molecule undergoes a transition from the ground electronic state to an excited electronic state. Then the dipole moment vector which appears in Eq. (23) is off-diagonal in the electronic state ( $k' \neq k''$ ), so that Eq. (21) is replaced by

$$M_{fi} = \int_0^{2\pi} \int_0^\pi Y_{j'm'}(\Theta, \Phi)^* Y_{j''m''}(\Theta, \Phi) \sin \Theta d\Theta d\Phi \int_0^\infty \chi_{v'j'} D_x^{(k'k'')}(\vec{R}) \chi_{v''j''} dR \quad (41)$$

where  $D_x^{(k'k'')}(\vec{R})$  is the off-diagonal electronic transition dipole moment vector of Eq. (9). This can be simplified, as in Eq. (23), to

$$M_{fi} = D_{v'j',v''j''}^{(k'k'')} \int_0^{2\pi} \int_0^\pi Y_{j'm'}(\Theta, \Phi)^* \cos \Theta Y_{j''m''}(\Theta, \Phi) \sin \Theta d\Theta d\Phi \quad (42)$$

where

$$D_{v'j',v''j''}^{(k'k'')} = \int_0^\infty \chi_{v'j'}^{(k')} D_x^{(k'k'')}(\vec{R}) \chi_{v''j''}^{(k'')} dR \quad (43)$$

Here, we have added electronic state indices to the vibrational wavefunctions, because these will be associated with different electronic potential curves.

In the case of pure rotation or vibration-rotation transitions within a given electronic state, the dipole-moment vector vanishes when the molecule is homonuclear. For electronic transitions, the dipole moment vector will vanish when the symmetry of the initial and final electronic wavefunctions is such that the off-diagonal matrix element of the electronic component of the dipole moment operator

$$\int dq_1 \int dq_2 \int dq_3 \dots \int dq_N \phi_{el}^{(k')}(q_1 q_2 q_3 \dots q_N)^* \left[ -\sum_{n=1}^N q_n \right] \phi_{el}^{(k'')}(q_1 q_2 q_3 \dots q_N) \quad (44)$$

vanishes, where the integration is over all the electrons.

## G. Selection Rules: Electronic Transitions

For diatomic molecules this imposes additional *electronic* selection rules, namely

$$\Lambda' = \Lambda, \Lambda' \pm 1$$

In addition, because the dipole-moment operator does not involve the spin, the integral over the electronic coordinates in Eq. (44) will vanish unless the total spin of the initial and final electronic states is identical, in other words

$$S' = S''$$

Finally, for homonuclear diatomic molecules, the expectation value of the dipole moment operator vanishes between an electronic state of  $\Sigma^-$  and a state of  $\Sigma^+$  symmetry, namely

$$\Sigma^- \leftrightarrow \Sigma^+$$

nor will transitions occur in which the  $g/u$  symmetry is unchanged

$$g \leftrightarrow g, u \leftrightarrow u$$

For electronic transitions the rotational selection rules are identical to Eq. (27) for transitions in which both electronic states are  $\Sigma$  states and are thus cylindrically symmetric. For other cases, a Q-branch ( $j' = j''$ ) will occur.

Vibrational selection rules will be imposed by the integral over  $R$  of Eq. (43). As we have done before, we expand the transition dipole moment function  $D^{(k'k'')}(R)$  in a power series, and retain, initially, only the first term

$$\begin{aligned} D^{(k'k'')}(R) &= D^{(k'k'')}(R_0) + \left. \frac{dD^{(k'k'')}(R)}{dR} \right|_{R=R_0} (R - R_0) + \dots \\ &\approx D^{(k'k'')}(R_0) \end{aligned} \quad (45)$$

Here the origin for the Taylor series expansion might be the arithmetic or geometric average of the equilibrium bond distances ( $R_e$ ) in the electronic states  $k'$  and  $k''$ . We thus obtain

$$D_{v'j',v''j''}^{(k'k'')} \approx D^{(k'k'')}(R_0) \int_0^\infty \chi_{v'j'}^{(k')} \chi_{v''j''}^{(k'')} dR \approx D^{(k'k'')}(R_0) \int_0^\infty \chi_{v',j'=0}^{(k')} \chi_{v'',j''=0}^{(k'')} dR \quad (46)$$

The integral over  $R$  is just the overlap between the vibrational wavefunctions in the initial and final electronic states. The intensity of the transition will then be proportional to the square of this vibrational overlap, which is called a “[Franck-Condon factor](#)”.

**Problem 11** The vibrational constant and the equilibrium internuclear separation in the  $X^2\Sigma^+$  and  $A^2\Pi$  electronic states of  $N_2^+$  are listed in Table II. Use this information in writing

TABLE II. Spectroscopic constants for the two lowest states of  $N_2^+$ .

State	$\omega_e$ (cm <sup>-1</sup> )	$R_e$ (Å)
$A^2\Pi$	1903.7	1.1749
$X^2\Sigma^+$	2207.00	1.1164

a Matlab script to determine the  $6 \times 6$  matrix of vibrational overlaps in  $N_2^+$

$$\left\langle \chi_{v',j'=0}^{(A)} \left| \chi_{v'',j''=0}^{(X)} \right. \right\rangle$$

for  $0 \leq v', v'' \leq 5$ .

## H. Rotational Bands in Electronic Transitions

For an electronic transition, the energy gap is given by a straightforward extension of Eq. (38), namely, for the R branch

$$\begin{aligned} \Delta_E &\equiv \varepsilon_{k'v',j'=j''+1} - \varepsilon_{k''v''j''} \\ &= T_e^{(k')} - T_e^{(k'')} + \omega_e^{(k')}(v' + 1/2) - \omega_e^{(k'')}(v'' + 1/2) - \omega_e x_e^{(k')}(v' + 1/2)^2 \\ &\quad + \omega_e x_e^{(k'')}(v'' + 1/2)^2 + B_{v'}^{(k')}(j'' + 1)(j'' + 2) - B_{v''}^{(k'')}j''(j'' + 1) \end{aligned} \quad (47)$$

and, for the P branch

$$\begin{aligned} \Delta_E &\equiv \varepsilon_{k'v',j'=j''-1} - \varepsilon_{k''v''j''} \\ &= T_e^{(k')} - T_e^{(k'')} + \omega_e^{(k')}(v' + 1/2) - \omega_e^{(k'')}(v'' + 1/2) - \omega_e x_e^{(k')}(v' + 1/2)^2 \\ &\quad + \omega_e x_e^{(k'')}(v'' + 1/2)^2 + B_{v'}^{(k')}j''(j'' - 1) - B_{v''}^{(k'')}j''(j'' + 1) \end{aligned} \quad (48)$$

Here, the constant  $T_e$  is the energy at the bottom of the potential curve for each state. For the R branch, the rotational contribution to the energy is (skipping, for clarity, the electronic

state indices)

$$B_{v'}(j'' + 2)(j'' + 1) - B_{v''}j''(j'' + 1) = (B_{v'} - B_{v''})j''^2 + (3B_{v'} - B_{v''})j'' + 2B_{v'} \quad (49)$$

Often the bond order is higher in the lower state, so that bond length will be smaller (stronger bond) and, consequently, the rotational constant in the lower electronic state ( $B_{v''}$ ) will be larger. In this case, the rotational contribution to the energy gap will increase as the initial rotational quantum number increases, but eventually, because of the quadratic term in Eq. (49) go through a maximum and then decrease. This is called a “band head”.

For a typical diatomic radical, Table III lists the spectroscopic constants for the  $X^2\Sigma^+$  and  $B^2\Sigma^+$  states. Figure 9 shows the simulated stick spectrum for the  $v' = 5 \leftarrow v'' = 0$

TABLE III. Spectroscopic constants for the two lowest  $^2\Sigma^+$  states of a model diatomic radical ( $\text{cm}^{-1}$ ).

State	$T_e$	$\omega_e$	$\omega_e x_e$	$v$	$B_v$
$B^2\Sigma^+$	25722	2163.9	20.2	5	1.7234
$X^2\Sigma^+$	0	2068.59	13.087	0	1.8997

band in the  $B^2\Sigma^+ \leftarrow X^2\Sigma^+$  transition of the this diatomic which occurs at  $\approx 2780 \text{ \AA}$  (in the near UV). The band head in the R branch is clearly visible. The right-hand panel of this figure shows the effect of broadening, obtained by convolution with a Gaussian instrument function of width  $4 \text{ cm}^{-1}$  FWHM. The closely-spaced lines in the R branch are now no longer resolvable, while structure in the P branch is still apparent, reflecting the sparser pattern of lines in the P branch.

**Problem 12** The lower R- and P-branch lines of an unknown diatomic molecule are listed in the following table, along with the relative intensities of the individual lines. Plot the stick spectrum. Indicate on your plot the rotational assignment of each line ( $j' \leftarrow j''$ ). Determine the rotational constants for the upper and lower state:  $B'$  and  $B''$ . Finally, determine the temperature of the gas. *Hint:* Remember from Eqs. (35) and (40) that the relative intensities of a  $P$  and  $R$  branch lines originating from rotational level  $j''$  are  $j'' : (j'' + 1)$ .

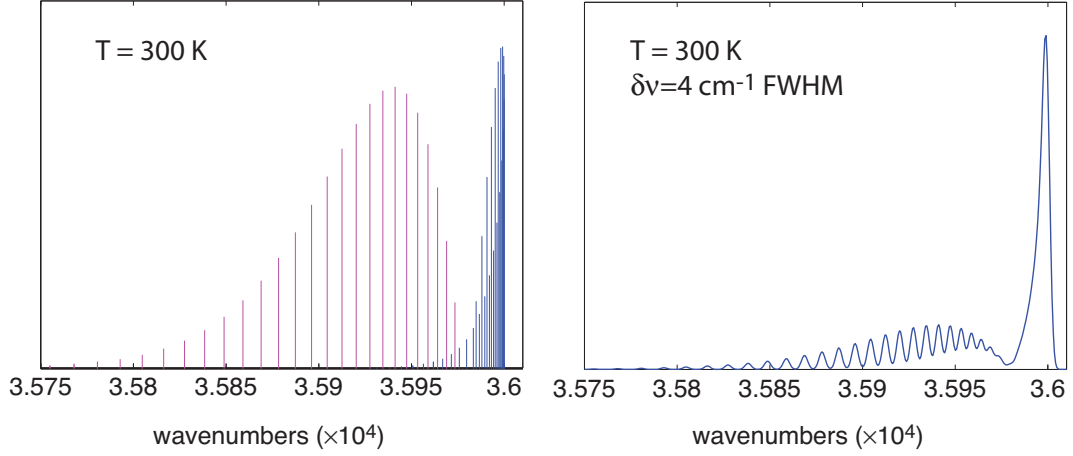


FIG. 9. Simulated stick spectrum (left panel) of the  $v' = 5 \leftarrow v'' = 0$  band in the  $B^2\Sigma^+ \leftarrow X^2\Sigma^+$  transition of the model diatomic. In the right panel appears the same spectrum but broadened by convoluting with a Gaussian instrument function with FWHM of  $4 \text{ cm}^{-1}$ .

TABLE IV. Line positions.

Line position ( $\text{cm}^{-1}$ )	relative intensity
35958.8538	5.85
35964.0636	6.00
35968.9208	5.49
35973.4253	4.25
35977.5773	2.34
35984.8235	2.46
35987.9177	4.69
35990.6594	6.37
35993.0484	7.32
35995.0848	7.50

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- [1] For light in which the electric field precesses around the direction of propagation – called circularly polarized light – the selection rule is  $\Delta m = \pm 1$ .
- [2] A. R. Edmonds, *Angular Momentum in Quantum Mechanics*, 2nd edition, third printing (Princeton University Press, Princeton, 1974).
- [3] In reality, the dipole moment of a molecule in vibration-rotation state  $vj$  is the average, over the vibrational wavefunction  $\chi_{vj}(R)$ , of the dipole moment function. In practice, this expectation value differs very little from  $D^{(k)}(R_e)$ .